

Conjugated Systems

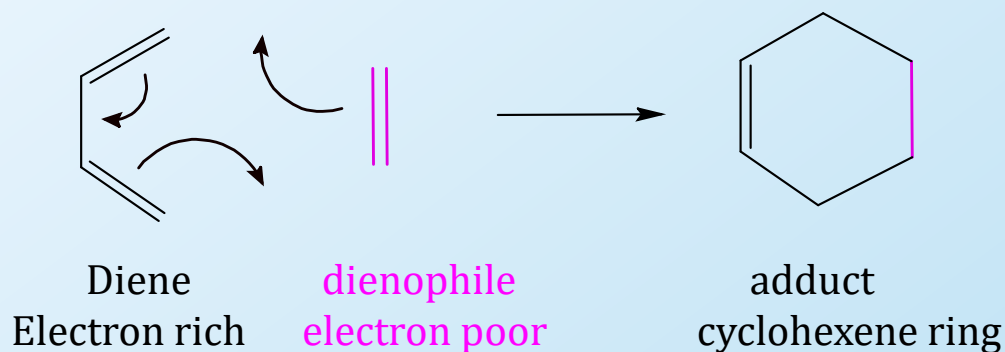
3 - Diels Alder Reactions

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Diels-Alder Reaction

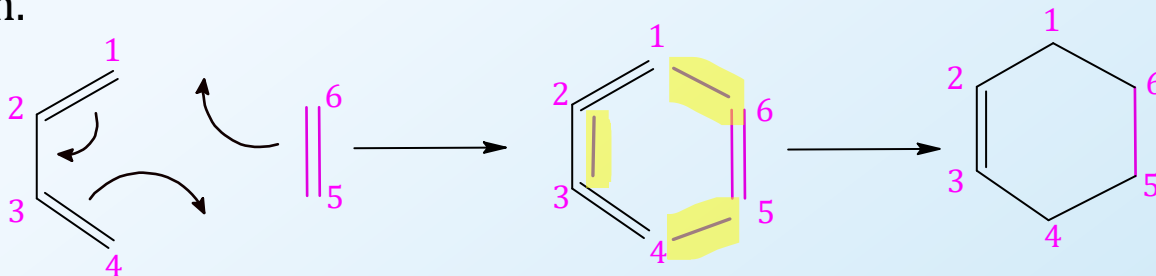
Diels Alder reaction was discovered by Otto Diels, Kurt Alder for which they won the Nobel prize in 1950.

- The reaction is an addition of a conjugate diene with alkenes to form a six-membered cyclic compound.
- The formation of the ring involves no intermediate (concerted formation of two bonds).
- The conjugated system is the **diene** which reacts with a **dienophile** (a double bonded system) to give an **adduct**/product.



Mechanism - Concerted

There is no clear nucleophile or electrophile. Reaction arrow starts from any one double bond to form new bonds. The blue/yellow highlighted lines in the reaction below show the new bonds forming, all at the same time. This is a concerted mechanism.



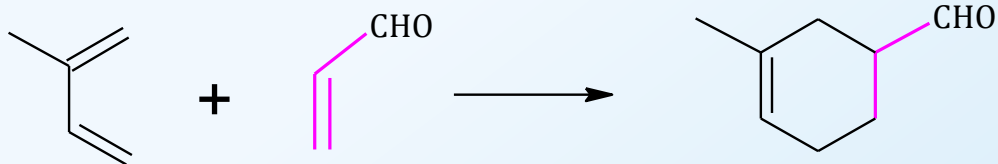
This reaction can be seen as an addition of a 4 + 2 system – the 4 C is the diene and the 2 C is the dienophile. The adduct will always be a 6 membered ring structure depending on what atoms are on the 4 + 2 system.

Examples of Diels-Alder Reactions

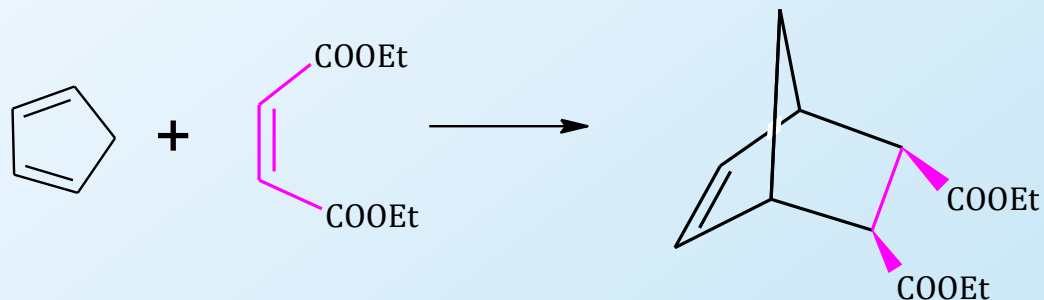
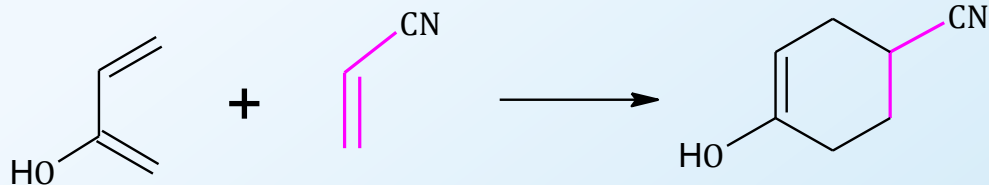
Diene

Dienophile

Adduct

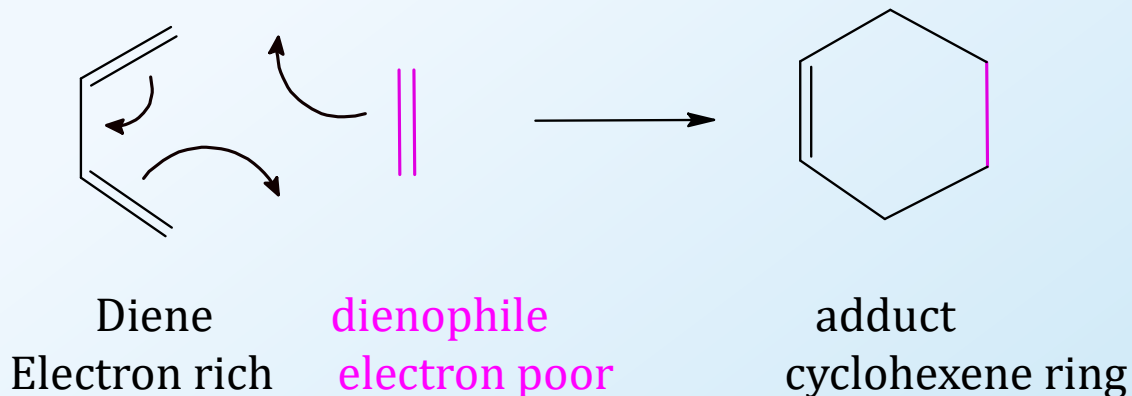


No ring in diene or dienophile:
One cyclohexene ring in product.



One ring in diene:
One cyclohexene ring in product + one more ring
Bicyclic product.

Dienes and Dienophiles

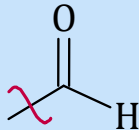
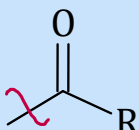
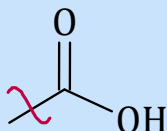
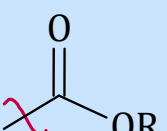
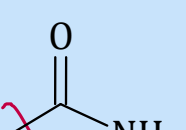
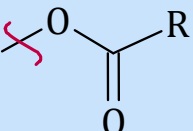
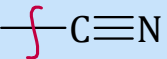


Diene	Dienophile
<ul style="list-style-type: none">• The diene component.• Is more effective when it is electron rich.• It can be made more electron rich by adding more electron donating groups.	<ul style="list-style-type: none">• The alkene component.• Is more effective if it is electron poor.• It can be made more electron poor by adding groups that are electron withdrawing.

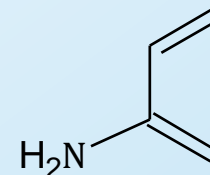
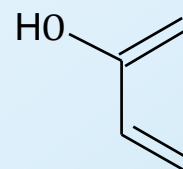
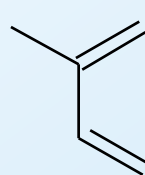
Groups on Dienes and Dienophile

For Dienes

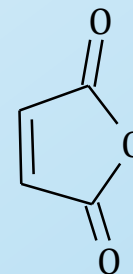
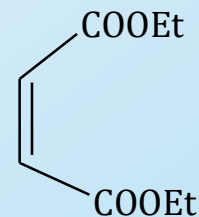
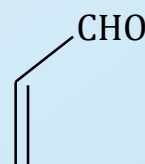
For Dienophiles

Electron Donating Groups	Electron Withdrawing Groups
-R (alkyl groups)	Aldehyde 
-OH (alcohol)	Ketone 
-OR (ether)	Acid 
-NH ₂ (amine)	Ester 
-Ph (phenyl)	Amide 
Ester 	Nitro -NO ₂
	Nitrile 

Some effective Dienes

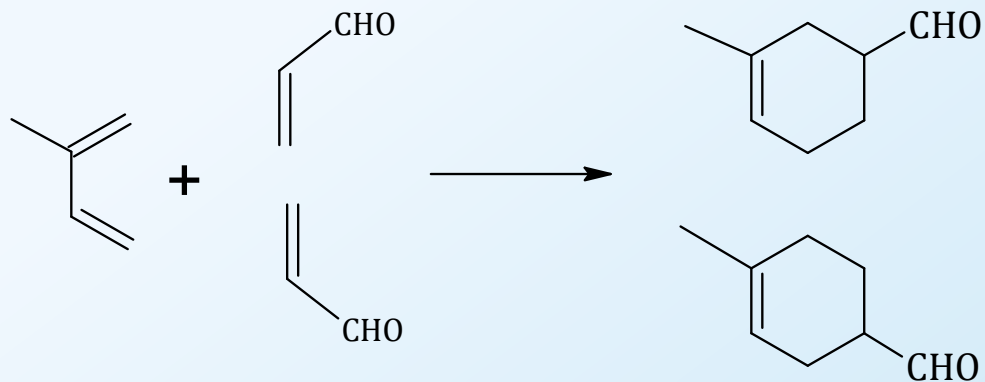


Some effective Dienophiles



Reactant Orientation and 4 + 2 System

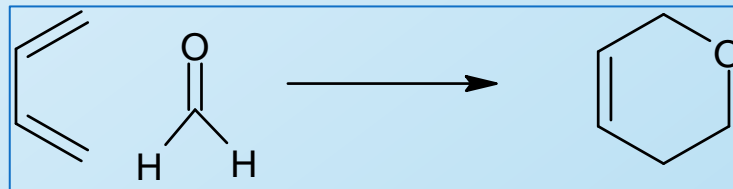
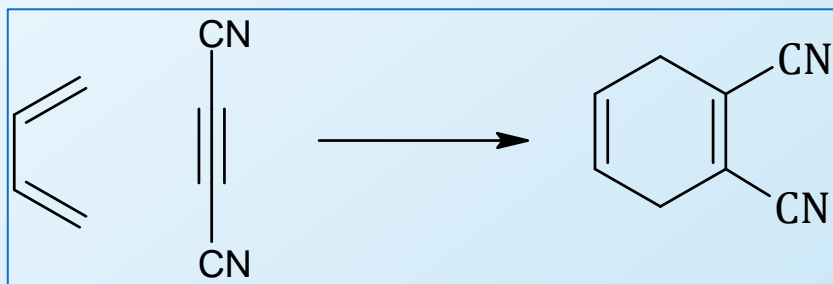
In Diels Alder reactions the diene is generally written first followed by the dienophile. It is helpful to visualize the product and keep things simple. When we write the dienophile, don't flip it to write the product. It does not mean that the second product will not form, it will; but we avoid forming it by selecting dienophiles that don't give multiple products.



Will form if dienophile is written as on top.

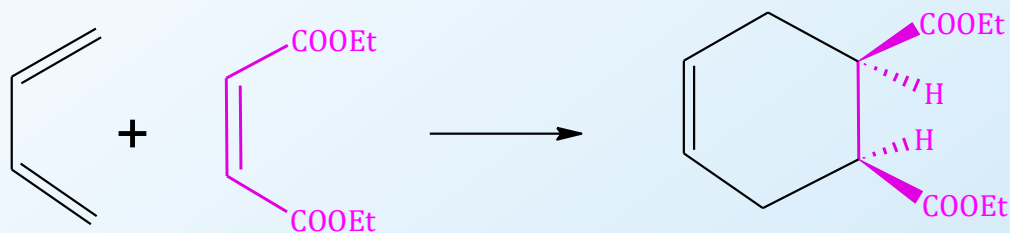
Will form if dienophile is written as bottom one.

Here are a couple examples of some 4+2 systems in DA reactions where dienophile looks different.

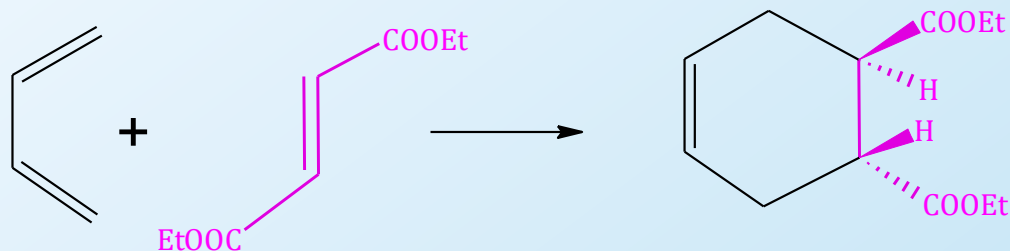


Stereospecificity in Diels-Alder Reaction

Stereospecificity means that when a cis dienophile is used the product will have those substituents in the cis stereochemistry, and if the dienophile is trans then product will also have trans stereochemistry. In both cases the enantiomer will also form.



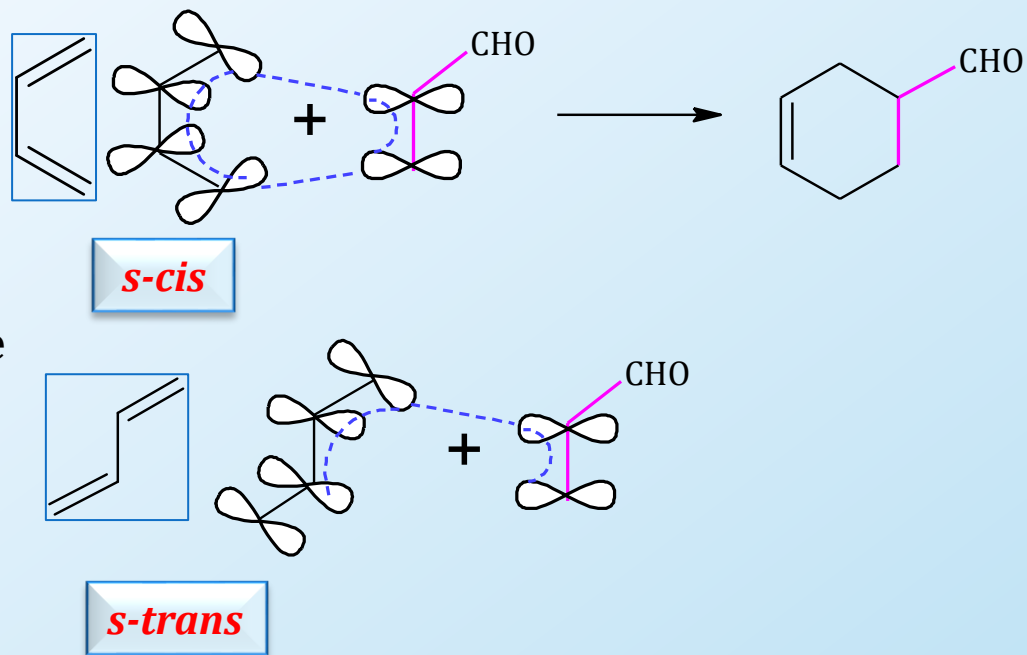
Cis dienophile gives a cis product



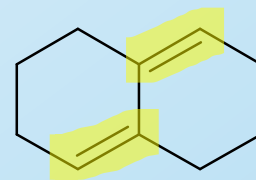
Trans dienophile gives a trans product

Conformation of the Diene

- The relative positions of the two double bonds in the diene are “*s-cis*” or “*s-trans*” to each other about the single bond.
- In *s-cis* the double bonds are on the same side. And in the *s-trans* the double bonds are on the opposite side of the single bond.
- Being in the same plane maximizes pi orbital overlap hence dienes react in the *s-cis conformation* in the Diels-Alder reaction.



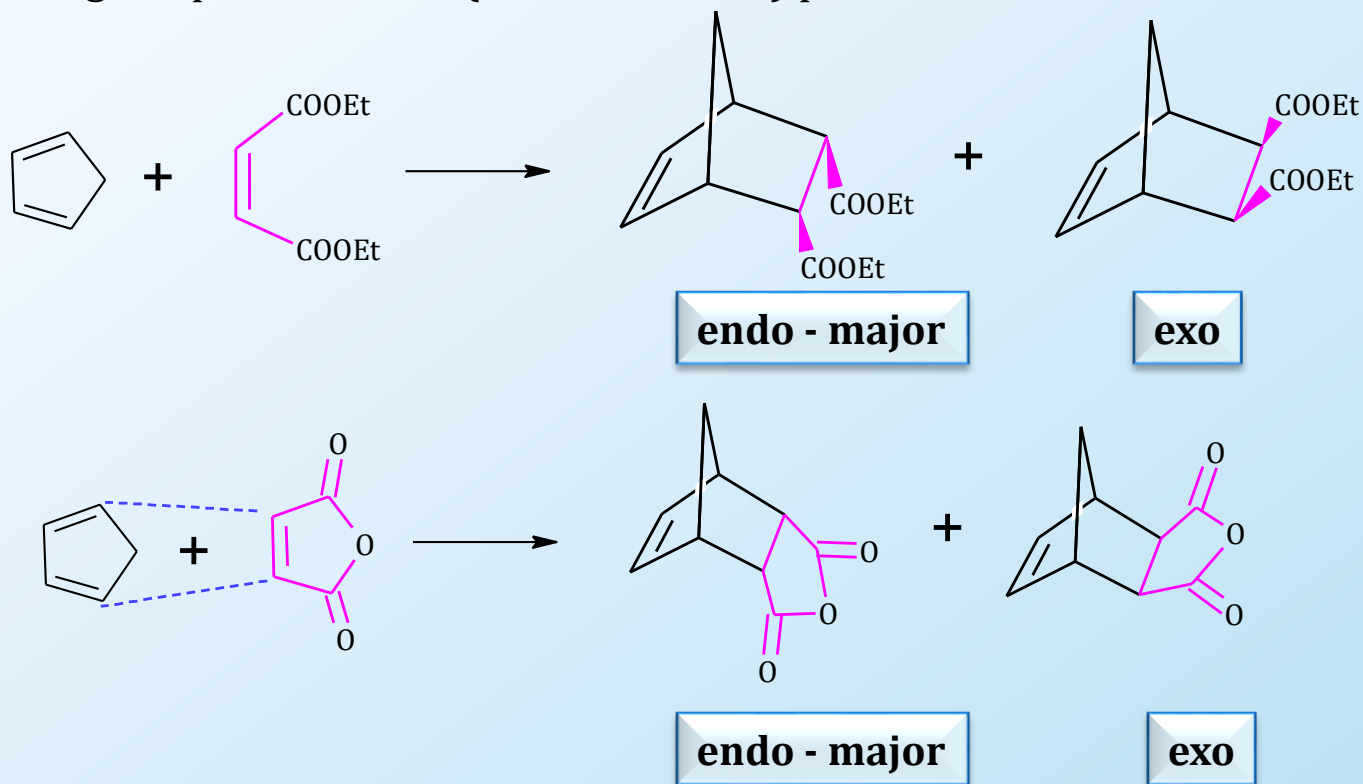
Some compounds have restricted rotation and thus the double bonds are locked into position to be unreactive in the *s-trans* position as shown in the example on the right.



Regioselectivity of Diels-Alder Reaction

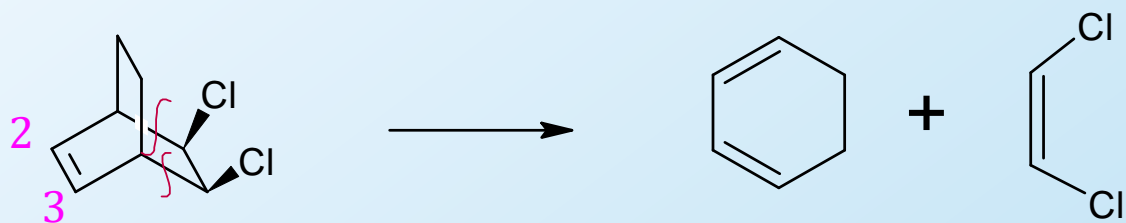
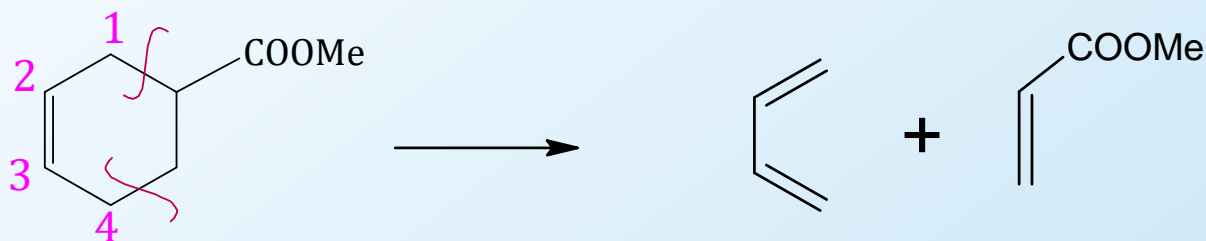
Endo and **exo** indicate relative stereochemistry in bicyclic structures. Endo products have the substituents going towards the bicyclic ring where there is less steric hinderance. In **exo** the substituents are facing outside the bicyclic ring causing steric hinderance with the bridging hydrogens.

Reactants align to produce *endo* (rather than *exo*) product.



Retrosynthesis

To determine the diene and dienophile required for an adduct, identify the double bond and label it as 2,3 and then find the diene by numbering the other carbons (1,4). The 4+2 system can then help you identify the two new bonds formed during Diels Alder reaction.



Key Concepts

- Diene – Dienophile.
- Electron withdrawing and donating groups.
- Stereoselectivity.
- Regioselectivity.
- Conformation of the diene.